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(54) **GRANULES A BASE DE DIOXYDE DE TITANE PYROGENE, UN PROCEDE POUR LEUR PREPARATION ET LEUR UTILISATION**

(54) **GRANULES BASED ON PYROGENIC TITANIUM DIOXIDE, A PROCESS FOR PREPARING THEM AND THEIR USE**

(57) Granules based on titanium dioxide with the characteristics: Average particle diameter: 10 to 150 µm BET surface area: 25 to 100 m^2/g PH 3 to 6 Compacted density: 400 to 1,200 g/l They are prepared by dispersing titanium dioxide in water and spray-drying and silanisin. In the silanised form, the granules have the following characteristics: Average particle diameter: 10 to 160 µm BET surface area: 15 to 100 m^2/g pH: 3.0 to 9.0 Compacted density: 400 to 1,200g/l Carbon content: 0.3 to 12.0 wt.% The granules are used, inter alia, as catalyst supports, in cosmetics, as sun screens, in silicone rubber, in toning powder, in lacquers and colorants, as grinding and polishing agents and as a raw material for producing glass and ceramics.

Abstract

Granules based on titanium dioxide with the characteristics:

Average particle diameter:	10 to 150 µm
BET surface area:	25 to 100 m^2/g
pH:	3 to 6
Compacted density:	400 to 1,200 g/l

They are prepared by dispersing titanium dioxide in water and spray-drying and silanisin.

In the silanised form, the granules have the following characteristics:

Average particle diameter:	10 to 160 µm
BET surface area:	15 to 100 m^2/g
pH:	3.0 to 9.0
Compacted density:	400 to 1,200 g/l
Carbon content:	0.3 to 12.0 wt.%

The granules are used, inter alia, as catalyst supports, in cosmetics, as sun screens, in silicone rubber, in toning powder, in lacquers and colorants, as grinding and polishing agents and as a raw material for producing glass and ceramics.

Granules based on pyrogenic titanium dioxide, a process for preparing them and their use

The invention provides granules based on pyrogenic titanium dioxide, the process for preparing them and the use thereof.

It is known that pyrogenic titanium dioxide can be prepared from $TiCl_4$ by high temperature or flame hydrolysis (Ullmanns Enzyklopädie der technischen Chemie, 4th edition, vol. 21, page 464 (1982)).

Pyrogenic titanium dioxide is characterised by extremely finely divided particles, a high surface area (BET), very high purity, spherically shaped particles and a lack of pores. As a result of these properties, pyrogenic titanium dioxide is increasingly being considered as a support for catalysts (Dr. Koth et al., Chem. Ing. Techn. **52**, 628 (1980)). For this application, pyrogenic titanium dioxide is shaped in a mechanical manner using, for example, tabletting machines.

Thus, there is the object of producing spray-dried granules of pyrogenic titanium dioxide which can be used as a catalyst support.

The invention provides granules based on pyrogenic titanium dioxide with the following physico-chemical characteristics:

Average particle diameter:	10 to 150 µm
BET surface area:	25 to 100 m^2/g
pH:	3 to 6
Compacted density:	400 to 1,200 g/l

Granules according to the invention can be prepared by dispersing pyrogenic titanium dioxide in water, spray-drying.

The invention also provides granules based on pyrogenic titanium dioxide with the following physico-chemical characteristics:

Average particle diameter:	10 to 160 µm
BET surface area:	15 to 100 m^2/g
pH:	3.0 to 9.0
Compacted density:	400 to 1,200 g/l
Carbon content:	0.3 to 12.0 wt.%

Granules according to the invention can be prepared by dispersing pyrogenic titanium dioxide in water, spray-drying then silanising the product. Halogenated silanes, alkoxysilanes, silazanes and/or siloxanes are used for silanising.

The following substances may be used in particular as halogenated silanes:

Halogenated organosilanes of the type $X_3Si(C_nH_{2n+1})$

X = Cl, Br

n = 1 - 20

Halogenated organosilanes of the type $X_2(R')Si(C_nH_{2n+1})$

X = Cl, Br

R' = alkyl

n = 1 - 20

Halogenated organosilanes of the type $X(R')_2Si(C_nH_{2n+1})$

X = Cl, Br

R' = alkyl

$n = 1 - 20$

Halogenated organosilanes of the type $X_3Si(CH_2)_m-R'$

$X =$ Cl, Br

$m =$ 0, 1 - 20

$R' =$ alkyl, aryl (e.g. $-C_6H_5$)

$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$

$-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,

$-OOC(CH_3)C=CH_2$

$-OCH_2-CH(O)CH_2$

$-NH-CO-N-CO-(CH_2)_5$

$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$

$-S_x-(CH_2)_3Si(OR)_3$

Halogenated organosilanes of the type $(R)X_2Si(CH_2)_m-R'$

$X =$ Cl, Br

$R =$ alkyl

$m =$ 0, 1 - 20

$R' =$ alkyl, aryl (e.g. $-C_6H_5$)

$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$

$-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,

$-OOC(CH_3)C=CH_2$

$-OCH_2-CH(O)CH_2$

$-NH-CO-N-CO-(CH_2)_5$

$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$

$-S_x-(CH_2)_3Si(OR)_3$

Halogenated organosilanes of the type $(R)_2XSi(CH_2)_m-R'$

$X =$ Cl, Br

$R =$ alkyl

$m =$ 0, 1 - 20

$R' =$ alkyl, aryl (e.g. $-C_6H_5$)

$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$

$-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,

$-OOC(CH_3)C=CH_2$

$-OCH_2-CH(O)CH_2$

$-NH-CO-N-CO-(CH_2)_5$
$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$
$-S_x-(CH_2)_3Si(OR)_3$

The following substances may be used in particular as alkoxysilanes:

Organosilanes of the type $(RO)_3Si(C_nH_{2n+1})$
R = alkyl
n = 1 - 20

Organosilanes of the type $R'_x(RO)_ySi(C_nH_{2n+1})$
R = alkyl
R' = alkyl
n = 1 - 20
x+y = 3
x = 1, 2
y = 1, 2

Organosilanes of the type $(RO)_3Si(CH_2)_m-R'$
R = alkyl
m = 0, 1 - 20
R' = alkyl, aryl (e.g. $-C_6H_5$)
$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$
$-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,
$-OOC(CH_3)C=CH_2$
$-OCH_2-CH(O)CH_2$
$-NH-CO-N-CO-(CH_2)_5$
$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$
$-S_x-(CH_2)_3Si(OR)_3$

Organosilanes of the type $(R'')_x(RO)_ySi(CH_2)_m-R'$
R" = alkyl x+y = 3
x = 1, 2
y = 1, 2
R' = alkyl, aryl (e.g. $-C_6H_5$)

$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$

$-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,

$-OOC(CH_3)C=CH_2$

$-OCH_2-CH(O)CH_2$

$-NH-CO-N-CO-(CH_2)_5$

$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$

$-S_x-(CH_2)_3Si(OR)_3$

The silane Si 108 $[(CH_3O)_3-Si-C_8H_{17}]$ trimethoxyoctylsilane may preferably be used as the silanising agent.

The following substances may be used in particular as silazanes:

Silazanes of the type $R'R_2Si-\underset{\substack{|\\ H}}{N}-SiR_2R'$

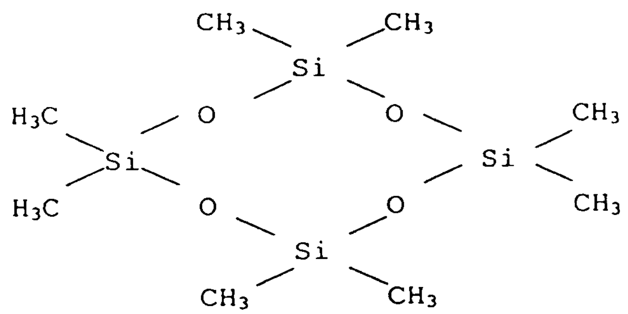
R = alkyl

R' = alkyl, vinyl

and also, for example, hexamethyldisilazane.

The following substances may be used in particular as siloxanes:

Cyclic polysiloxanes of the types D 3, D 4, D 5,
e.g. octamethylcyclotetrasiloxane = D 4



Polysiloxanes or silicone oils of the type

$$Y\text{-}O\text{-}\left[\left[\begin{array}{c}R\\|\\Si\text{-}O\\|\\R'\end{array}\right]_m\left[\begin{array}{c}R''\\|\\Si\text{-}O\\|\\R'''\end{array}\right]_n\text{-}Y\right]_u$$

$m = 0, 1, 2, 3, \ldots \infty$
$n = 0, 1, 2, 3, \ldots \infty$
$u = 0, 1, 2, 3, \ldots \infty$

Y = CH_3, H, C_nH_{2n+1}, n = 1 - 20
Y = $Si(CH_3)_3$, $Si(CH_3)_2H$
$Si(CH_3)_2OH$, $Si(CH_3)_2(OCH_3)$
$Si(CH_3)_2(C_nH_{2n+1})$, n = 1 - 20

R = alkyl, aryl, $(CH_2)_n-NH_2$, H
R' = alkyl, aryl, $(CH_2)_n-NH_2$, H
R" = alkyl, aryl, $(CH_2)_n-NH_2$, H
R''' = alkyl, aryl, $(CH_2)_n-NH_2$, H

The carbon content of granules according to the invention may be 0.3 to 12.0 wt.%.

The dispersion in water may have a titanium dioxide concentration of 3 to 25 wt.%.

Organic auxiliary substances may be added to the dispersion in order to increase the stability of the

dispersion and to improve the particle morphology after spray-drying.

The following auxiliary substances may be used, for example:
polyalcohols, polyethers, surfactants based on fluorinated hydrocarbons, alcohols.

Spray-drying may be performed at a temperature of 200 to 600°C. Spinning disc atomisers or nozzle atomisers may be used.

Silanising may be performed using the halogenated silanes, alkoxysilanes, silazanes and/or siloxanes described above, wherein the silanising agent may optionally be dissolved in an organic solvent such as, for example, ethanol.

The silane Si 108 [$(CH_3O)_3$-Si-C_8H_{17}] trimethoxyoctylsilane may preferably be used as the silanising agent.

Silanising may be performed by spraying the granules with silanising agent at room temperature and then thermally treating the mixture at a temperature of 105 to 400°C for a period of 1 to 6 h.

An alternative method of silanising the granules may be performed by treating the granules with the silanising agent in vapour form and then thermally treating the mixture at a temperature of 200 to 800°C for a period of 0.5 to 6 h.

Thermal treatment may be performed under a protective gas such as, for example, nitrogen.

Silanising may be performed continuously or batchwise in heatable mixers and dryers with spray devices. Suitable

devices may be, for example: plough bar mixers, disc dryers, fluidised bed dryers or moving bed dryers.

The physico-chemical parameters of the granules, such as the specific surface area, particle size distribution, compacted density and pH, may be modified within the limits given above by varying the substances used and the conditions used during spraying, heating at constant temperature and silanising.

Titanium dioxide granules according to the invention have the following advantages:
The flow behaviour is better than non-spray-dried titanium dioxide.
Incorporation into organic systems is easier.
Dispersion is simpler.
No additional auxiliary substances are required for granulation.
Titanium dioxide granules according to the invention have a defined particle size, unlike non-spray-dried titanium dioxide which does not have a defined agglomerate size.
Titanium dioxide granules according to the invention can be handled in a dust-free manner.
Lower packaging costs are required for transportation due to the high compacted density.
Titanium dioxide granules according to the invention can be used as a catalyst support.
Non-spray-dried titanium dioxide is not suitable for this purpose because, for example, it is carried out of a fluidised bed.

Granules according to the invention may be used as a support for catalysts, and also in cosmetics, as a sunscreen, in silicone rubber, in toning powder, in lacquers and colorants, as a grinding and polishing agent and as a raw material for producing glass and ceramics.

Examples

A titanium dioxide P25 with the following physico-chemical characteristics is used as a pyrogenic titanium dioxide. It is disclosed in the series of documents called Pigments, no. 56 "Hochdisperse Metalloxide nach dem Aerosilverfahren", 4th edition, February 1989, Degussa AG.

	Titanium dioxide P25
CAS no.	13463-67-7
Behaviour in water	hydrophilic
Appearance	loose white powder
BET surface area [1] m^2/g	50 ± 15
Average size of primary particles nm	21
Compacted density [2] g/l	about 100
Specific weight [10] g/l	about 3.7
Loss on drying [3] on leaving supplier (2 h at 105°C) %	< 1.5
Loss on ignition [4] [7] (2 h at 1000°C)	< 2
pH [5] (in 4% aqueous dispersion)	3-4
SiO_2 [8]	< 0.2
Al_2O_3 [8]	< 0.3
Fe_2O_3 [8]	< 0.01
TiO_2 [8]	>99.5
ZrO_2 [8]	-
HfO_2 [8]	-
HCl [9]	< 0.3
Sieve residue [6] (Mocker's method, 45 µm) %	< 0.05

1) according to DIN 66131
2) according to DIN ISO 787/XI, JIS K 5101/18 (not sieved)
3) according to DIN ISO 787/II, ASTM D 280, JIS K 5101/21
4) according to DIN 55921, ASTM D 1208, JIS K 5101/23
5) according to DIN ISO 787/IX; ASTM D 1208; JIS K 5101/24
6) according to DIN ISO 787/XVIII; JIS K 5101/20
7) with respect to substance dried for 2 h at 105°C
8) with respect to substance ignited for 2 h at 1000°C
9) HCl content is component of loss on ignition
10) determined with an air comparison density bottle

The titanium dioxides are prepared by spraying a volatile titanium compound into an oxyhydrogen flame formed from hydrogen and air. In most cases, titanium tetrachloride is used. This substance hydrolyses under the effect of the water being produced during the oxyhydrogen gas reaction to give titanium dioxide and hydrochloric acid. After leaving the flame, the titanium dioxide enters a so-called coagulation zone in which the titanium dioxide primary particles and primary aggregates agglomerate. The product, present at this stage as a kind of aerosol, is separated from the gaseous accompanying substances in cyclones and is then post-treated with moist hot air.

The particle sizes of the titanium dioxides may be varied by varying the reaction conditions such as, for example, temperature of the flame, proportion of hydrogen or oxygen, amount of titanium tetrachloride, residence time in the flame or the length of the coagulation zone.

The BET surface area is determined using nitrogen in accordance with DIN 66 131.

<u>The compacted volume</u> is determined in a similar way to that described in ASTM D 4164-88.

<u>Equipment</u>: Compacted volume meter STA V 2003 from the Engelsmann Co., in accordance with DIN 53194, para. 5.2 b-f
250 ml measuring cylinder, graduation mark every 2 ml
Balance with max. error limit of ± 0.1 g

<u>Performing the determination</u>

Set the counter on the compacted volume meter to 1000 strokes.

Tare the measuring cylinder.

Fill measuring cylinder with granules up to the 250 ml mark.

Note down the weight (± 0.1 g).

Clamp the measuring cylinder in the compacted volume meter and switch the instrument on.

End of compacting → instrument automatically stops after 1000 strokes.

Read the compacted bulk volume accurately, to 1 ml.

Calculation

E: weight of granules in g

V: volume read off in ml

W: water content in wt.% (determined in accordance with test instructions P001)

$$\text{Compacted density} = \frac{E \times (100 - W)}{V \times 100}$$

The pH is determined in 4 % strength aqueous dispersion, in the case of hydrophobic catalyst supports in water:ethanol 1:1.

Preparing granules according to the invention

The pyrogenic titanium dioxide is dispersed in fully deionised water. A dispersing apparatus is used which operates on the rotor/stator principle. The dispersions being produced are spray-dried. Deposition of the final product is achieved using a filter or a cyclone.

The spray-dried and optionally heated granules are initially introduced into a mixer to be silanised and are

sprayed optionally first with water and then with the silanising agent, under intense mixing. After completion of the spraying procedure, mixing is continued for 15 to 30 min and then the mixture is heated at a constant temperature of 100 to 400°C for 1 to 4 h.

The water used may be acidified with an acid, for example hydrochloric acid, until the pH is 7 to 1. The silanising agent used may be dissolved in a solvent such as, for example, ethanol.

Table 1

Data relating to spray-drying aqueous TiO_2P25 dispersions

Example	**Amount of H_2O [kg]**	**Amount of TiO_2P25 [kg]**	**Atomised using**	**Speed of atomising disc [rpm]**	**Operating temp. [°C]**	**Vent air temp. [°C]**	**Deposition**
1	10	1.5	disc	35 000	345	100	cyclone
2	10	1.5	disc	45 000	370	105	cyclone
3	10	1.5	disc	20 000	350	95	cyclone
4	10	2.5	disc	15 000	348	100	cyclone
5	100	15	2-fluid nozzle	---	445	130	filter
6	100	15	disc	10 000	450	105	filter
7	10	2.5	disc	20 000	348	105	cyclone
8	10	1.5	disc	15 000	348	105	cyclone
9	10	2.5	disc	35 000	300	105	cyclone

Table 2

Physico-chemical data of spray-dried products

Example	BET surface area [m^2/g]	Compacted density [g/l]	pH	d_{50} value (Cilas) [µm]	Loss on drying [%]	Loss on ignition [%]
1	51	641	3.9	14.6	0.9	0.9
2	50	612	3.7	10.6	0.8	1.0
3	52	680	3.5	25.0	0.8	1.0
4	51	710	3.7	43.6	0.8	1.2
5	52	660	4.0	17.1	0.9	0.9
6	53	702	3.9	27.5	0.9	0.9
7	50	708	3.5	26.7	1.1	0.6
8	53	696	3.9	30.1	1.0	0.9
9	49	640	3.7	16.0	0.7	0.8

Table 3

Data relating to hydrophobing titanium dioxide granules in accordance with example 6

Example	Amount of P25/7 [kg]	Hydrophobing agent	Amount of hydrophobing agent [kg]	Amount of H_2O [kg]	Constant temperature [°C]	Heating time hours
10	2	Si 108	0.2	0.05	120	2
11	2	Si 108	0.3	0.05	120	2
12	3.15	silicone oil	0.2	0	350	2
13	3.15	silicone oil	0.3	0	350	15

Table 4

Physico-chemical data of hydrophobised titanium dioxide granules in accordance with example 6

Example	BET surface area [m^2/g]	Carbon content [%]	Compacted density [g/l]	pH	Loss on drying [%]	Loss on ignition [%]	d_{50} value (Cilas) [µm]
10	36	3.9	848	3.1	0.2	4.2	29.8
11	30	5.5	873	3.2	0.4	6.1	28.7
12	32	2.1	768	3.6	0	1.9	30.2
13	25	3.3	883	3.9	0	4.4	28.1

Claims

1. Granules based on pyrogenic titanium dioxide with the following physico-chemical characteristics:

Average particle diameter:	10 to 150 µm
BET surface area:	25 to 100 m^2/g
pH:	3 to 6
Compacted density:	400 to 1,200 g/l

2. A process for preparing granules according to Claim 1, characterised in that pyrogenic titanium dioxide is dispersed in water and spray-dried.

3. Granules based on pyrogenic titanium dioxide with the following physico-chemical characteristics:

Average particle diameter:	10 to 160 µm
BET surface area:	15 to 100 m^2/g
pH:	3.0 to 9.0
Compacted density:	400 to 1,200 g/l
Carbon content:	0.3 to 12.0 wt.%

4. A process for preparing granules according to Claim 3, characterised in that pyrogenic titanium dioxide is dispersed in water and spray-dried and then silanised.

5. Use of granules according to Claims 1 and 3 as catalyst supports, and also in cosmetics, as sun screens, in silicone rubber, in toning powder, in lacquers and colorants, as grinding and polishing

agents and as a raw material for producing glass and ceramics.